KINETIC MODELING OF THE FORMATION OF POLYCYCLIC AROMATIC HYDROCARBONS

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1. INTRODUCTION

Growing evidence of the significant role of polycyclic aromatic hydrocarbons (PAH) in the formation of small particles such as soot in atmospheric aerosols and the known mutagenic or tumorigenic properties of at least some of them[1,2] necessitate a better understanding of the chemical growth process leading to larger and larger molecules. Combustion represents a major source of PAH and soot particles in the environment, therefore more efficient and cleaner combustion processes would lead to a significant reduction of pollution and to a more economic use of fossil fuels. Kinetic modeling can be expected to be a powerful tool for a better understanding of chemical processes responsible for PAH and utimately soot formation. A sufficiently developed model will finally allow the assessment of optimized operating conditions for practical combustion devices. In the recent years detailed kinetic models describing the formation of small and medium PAH have been developed and tested against experimental data obtained under well defined laboratory conditions such as shock tube pyrolysis[3,4] or premixed flames[5-11].

In the present work, two sets of experimental data obtained with different laboratory combustors, fuels and pressures are used in order to improve the reliability and in particular the detailed understanding of elementary reaction steps of a kinetic model developed recently for fuel rich benzene combustion under low pressure conditions[11].

2. APPROACH

A nearly sooting low pressure premixed, laminar, one-dimensional benzene/oxygen/argon flame (equivalence ratio $\phi = 1.8$, 30% argon, 50 cm s^{-1}, 2.67 kPa) for which large sets of experimental data[12,13] are available was modeled using the Premix code[14]. This flame has been studied by Bittner and Howard[12] using molecular beam sampling coupled to mass spectrometry (MBMS) to establish concentration profiles for stable species up to 202 amu and radicals up to 91 amu. The temperature profile was determined with a thermocouple taking into account heat losses by radiation. Because the measurements include unstable, often radical, intermediates the data provide valuable insights and have been used for different modeling studies focusing on a better understanding of benzene oxidation chemistry[5,6,9] and for the assessment of the first reaction steps of PAH growth[11]. The use of nozzle beam sampling followed by radical scavenging and subsequent analysis by gas chromatography coupled to mass sepctrometry, a technique developed and sucessfully used by Hausmann et al.[15], allowed Benish[13] to extend the data set to species up to 276 amu in the case of stable species and up to 201 amu for radicals.

The other experimental data used in the present work consist of concentration profiles of light gas species and PAH up to 300 amu measured for fuel rich $C_2H_4/O_2/N_2$ combustion ($\phi = 2.2$) in a jet-stirred-reactor/plug-flow reactor (JSR/PSR) system by means of gas chromatography operating at amospheric pressure[16,17]. The temperature was constant at 1630K in the JSR and 1630 K in the PFR. The outlet of the JSR was coupled to the inlet of the PFR. Kinetic models can be applied easily to both JSR and PFR which allows the comparison of model predictions to experimental data.

The parallel investigation of PAH formation under different conditions at low pressure, atmospheric pressure and different fuels, i. e., benzene and ethylene, is particularly challenging for a kinetic model. The present study is based on a recently published model tested for low pressure conditions[11] but with the rate constants of pressure-dependent chemically activated reactions, e. g., for benzene formation via the reaction of acetylene with 1-butadienyl radical[20], which have been systematically adapted to 1 atm using the QRRK (Quantum Rice-Ramsperger-Kassel) technique[21]. Thermodynamic data have been critically assessed and updated with available literature data or, in the case of poorly known PAH radicals, computed using *ab initio* techniques. Vibrational analysis performed on the optimized geometries allowed the determination of entropies and heat capacities while enthalpies of formation were determined by means of isodesmic reactions. Rate constants of reactions involved in the growth process have been investigated. The potential energy surfaces, including transition states, of the reactions phenyl + acetylene and of 1-naphthyl + acetylene have been explored. The resulting high pressure rate constants for the different elementary reactions followed by a QRRK treatement allowed the determination of "apparent" rate constants at different pressures and temperatures

describing the competing pathways. In the case of the reaction of 1-naphthyl with acetylene, as shown in Fig. 1, rate constants for the formation of 1-vinylnaphthalene, 1-napththylacetylene and acenaphtalene were determined and implemented in the kinetic model.
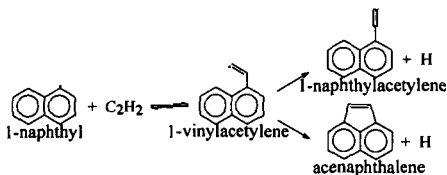

Fig. 1. Reaction pathways of 1-naphthyl + acetylene

3. RESULTS

a) Fuel Consumption and Formation of Main Products and Intermediates

A meaningful testing of a chemical reaction mechanism describing the growth of polycyclic aromatic hydrocarbons requires the correct prediction of key species which intervene in this process. The previously published kinetic model[1] showed good prediction capabilities for key products but also intermediate radicals such as H or OH compared to the MBMS data measured by Bittner and Howard[12]. In addition, the reliability of the model has been confirmed by means of the comparison of its predictions with experimental mole fraction profiles of stable species in a sooting low pressure premixed benzene/oxygen/argon flame (ϕ= 2.4, 5.33 kPa)[22]. However, an underprediction by a factor of $\approx$2.5 of the the peak mole fraction of acetylene was observed in the nearly sooting benzene flame studied in the present work while peak values of cyclopentadienyl (C_5H_5) and phenyl (C_6H_5) showed corresponding overpredictions[11]. A significant improvement of the predictions of these three species could be achieved by the addition of the oxidation of phenyl and phenoxy radicals to benzoquinone as suggested by Frank et al.[23] followed by the unimolecular decay and oxidation of benzoquinone to different C_6 and C_5 species leading ultimately to acetylene as discussed by Alzueta et al.[24]. Fig. 2 shows the predictions of the model developed in the present work for cyclopentadienyl and acetylene in comparison to the data of Bittner and Howard[11]. For the same flame, predictions and experimental data for benzene comsumption, CO_2 and water formation as well as the experimental temperature profile used for the model computation are summarized in Fig. 3. Also the update of the thermodynamic database, described above, contributed significantly to the improvement of the agreement between model predictions and experimental data.
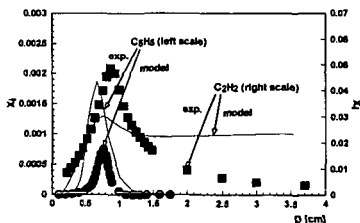

Fig 2. Model predictions and experimental data of acetylene and cyclopentadienyl in a nearly sooting premixed benzene/oxygen/argon flame (ϕ= 1.8, 2.67 kPa)[11].
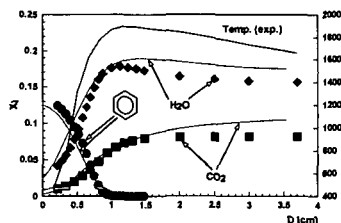
Fig 3. Model predictions and experimental data of Benzene, CO_2 and H_2O and experimental temperature profile in a nearly sooting premixed benzene/oxygen/argon flame (ϕ= 1.8, 2.67 kPa)[11].

A similar approach has been taken in order to check the prediction capability of the atmospheric pressure version of the model using ethylene combustion data from the JSR/PFR system operating at amospheric pressure[16,17]. The performance of the model was first tested for the comsumption of the reactant and the formation of key products and intermediates. Fig. 4 and 5 show the results of the model for ethylene, acetylene, H_2 and CO_2 in comparison with experimental data measured in the PFR at 1620K. In particular the excellent prediction of acetylene, a species assumed to be a key species in the formation process of PAH, is essential for the quality of the model but also the good agreements for ethylene consumption and CO_2 formation, representing the reactant and one of the main products, is encouraging. H_2 is only slightly underpredicted, another important finding because of the importance of hydrogen-abstraction reactions (R-H + H $\leftrightarrow$ R• + H_2) in the PAH growth process which may be affected by the location of the equilibrium on the reaction coordinate and therefore by the concentration of molecular hydrogen. Unfortunately, no experimental data on atomic hydrogen and other radical species are available due to the sampling technique used for the jet-stirred/plug-flow reactor system so that no check of equilibria exclusively based on experimental data has been possible.
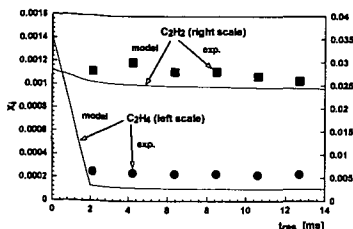
Fig 4. Model predictions and experimental data of ethylene and acetylene in a plug-flow reactor at 1620 K and 1 atm; JSR: $C_2H_4/O_2/N_2$ (ϕ= 2.2, 71.6% N_2, 1630K)[16,17].
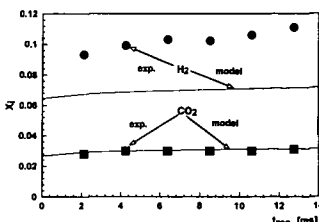
Fig 5. Model predictions and experimental data of H_2 and CO_2 in a plug-flow reactor at 1620 K and 1 atm; JSR: $C_2H_4/O_2/N_2$ (ϕ= 2.2, 71.6% N_2, 1630 K, 1 atm)[16,17].

b) Beginning of the Growth Process

The formation of polycyclic aromatic hydrocarbons (PAH) and of soot depends mainly on the the initial relative concentration of fuel and oxidizer, i. e., the equivalence ratio, reflecting the competition of oxidation with growth reactions. The latter becomes more favorable with increasing equivalence ratio. Assuming an essential role of a subsequent growth process from small to larger and larger PAH, the formation of the first aromatic species is of great interest. The importance of the formation of the first aromatic ring is confirmed by the order of the sooting tendencies: naphthalenes > benzenes > diolefins > monoolefins > paraffins[25]. Because of the presence of the first aromatic ring in the initial fresh gas mixture in the case of benzene combustion, the formation pathways for benzene will be discussed for ethylene combustion in the jet-stirred/plug-flow reactor system. Different pathways leading to the first aromatic ring, i. e., benzene or phenyl, have been discussed in the past[26] and are implemented in the present model. The analysis of the rates of production in the present work showed the reaction between
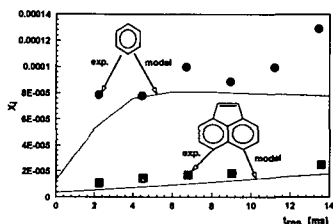

Fig 6. Model predictions and experimental data of benzene and acenaphthalene in a plug-flow reactor at 1620 K and 1 atm; JSR: $C_2H_4/O_2/N_2$ (ϕ= 2.2, 71.6% N_2, 1 atm)[16,17].

two propargyl (C_3H_3) being the dominant pathway but also the reaction of acetylene with a vinylacetylene radical (HCCHCCH) and of allene (CH_2CCH_2) with a C_3H_2 radical contributed significantly. It should be pointed out that no general conclusions can be drawn from these results because of the likely strong dependence of the relative contributions of the different pathways on experimental conditions such as temperature or fuel type. Nevertheless, the use of different pathways described previously in the literature in the present model allows an at least satisfactory agreement with experimental data as shown in Fig. 6.

c) Formation of the Second Aromatic Ring

Beginning with the first aromatic ring, mainly two pathways may lead to the formation of the next larger fused PAH, naphthalene. First, two subsequent H-abstraction/acetylene-addition steps[3,10] can lead to 1-naphthyl radicals, stabilized in the next step by recombination with atomic hydrogen. The other possibility consists of the reaction of two cyclopentadienyl radicals[7,11,27,28].
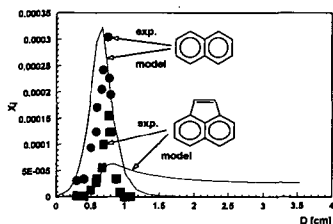

Fig 7. Model predictions and experimental data of naphthalene and acenaphthalene in a nearly sooting premixed benzene/oxygen/ argon flame (ϕ= 1.8, 2.67 kPa)[13].

The contribution of different pathways to the rate of formation of cyclopentadienyl radicals has been checked in the jet-stirred reactor and unimolecular decay of phenoxy was shown to be dominant. Napthalene formation has been investigated in both systems studied in the present work. A significant underprediction by a factor of $\approx$3 (not shown) was observed for the JSR/PFR system; the analysis of the rate of production revealed that nearly all naphthalene was formed via the hydrogen-abstraction/acetylene-addition pathway starting with benzene while no significant contribution of cyclopentadienyl radicals could be observed. A totally different picture was observed for the nearly sooting low pressure premixed

benzene flame. Confirming prior results[7,8,11], naphthalene formation is dominated by the reaction between two cyclopentadienyl moities. The comparison of the model prediction with the experimental naphthalene profile measured by Benish shows an excellent agreement (Fig. 7).

Recent measurements of radical concentration profiles in the benzene flame studied in this work[13] allowed the assessment of the role of hydrogen-abstraction/acetylene-addition pathway under the condition of this flame. In fact, the reaction of the phenylacetylene radical with acetylene to 1-napththyl (Fig. 8), represents the limiting step for the formation of 1-naphthyl. In contradiction to the good agreement observed for 2-naphthyl radicals (Fig. 10), the 1-naphthyl peak concentration is significantly underpredicted (Fig. 9). As shown in in Fig. 9, the total removal of the hydrogen-abstraction /acetylene addition pathway (Fig. 8) leads to a drastic increase of the 1-naphthyl peak mole fraction, in agreement with the experimental data, while a lack of sufficient consumption in the burnt gases is observed. Based on this observation, completed by tests of the impact of slight adjustments of thermodynamic and kinetic data, it seems likely that the 1-napthyl con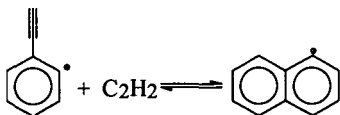centration, at least under the present conditions, is mainly governed by the equilibrium of the ring closure reaction (Fig. 8). Also the drastic decrease of the 1-naphthyl mole fraction at the end of the flame front seems to be strongly influenced by the reverse reaction (Fig. 9). Therefore, uncertaintenties on thermodynamic and kinetic data may be responsible for the underprediction of 1-naphthyl. This hypothesis is consistent with a much better agreement between the model prediction for the 2-naphthyl radical and the corresponding experimental profile (Fig. 10). 2-naphthyl is formed by hydrogen abstraction from naphthalene and is not directly involved in the above mentioned equilibrium.
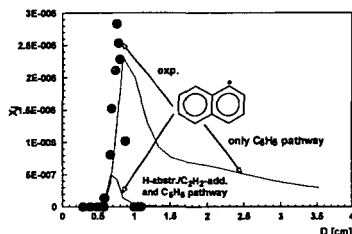
Fig 8. Napththalene formation via the hydrogen-abstraction/acetylene addition pathway.

$$+ \ C_2H_2 \rightleftharpoons$$

Fig 9. Model predictions and experimental data of 1-naphthyl in a nearly sooting premixed benzene/oxygen/argon flame (ϕ= 1.8, 2.67 kPa)[13]; use of complete model and after removal of H-abstraction/C$_2$H$_2$-addition pathway.
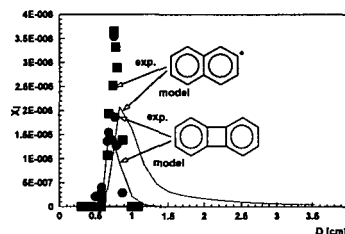
Fig 10. Model predictions and experimental data of 2-naphthyl and biphenylene in a nearly sooting premixed benzene/oxygen/argon flame (ϕ= 1.8, 2.67 kPa)[13].

d) Further Growth Process

Acenaphthalene, a PAH containing a five-membered ring, is usually an abundant species in the exhaust of combustion systems generating PAH. The comparison of model prediction with experimental data is shown for ethylene combustion in the JSR/PFR system (Fig. 6) as well as for low pressure benzene combustion (Fig. 7). A particular good agreement could be achieved in the JSR/PFR system, nethertheless also the significant underproduction of naphthalene in this system must be taken into account which leads to the assumption of an even too pronounced acenapthalene formation. The analysis of the net production rate of acenaphthalene shows a nearly exclusive formation via the reaction of acetylene with 1-naphthyl (Fig. 1), using the rate constant determined for 1 atm by means of the QRRK approach discussed above. A different situation has been observed in the case of low pressure premixed benzene combustion, in agreement with prior work[11], where the exclusive use of the reaction between 1-naphthyl and acetylene yields an underprediction of at least 20-fold. This finding confirms the conclusion of Hausmann et al.[15] that another, yet unknown, acenapthalene formation pathway exists. In the present work an additional acenaphthalene pathway has been suggested and implemented in the model. The isomerization of a biphenylene radical followed by hydrogen loss to acenaphthalene has been assumed and led to a significant improvement in the predictions of acenaphthalene but also biphenylene (Fig. 10), both of which species were measured by Benish[13]:

$$\rightleftharpoons \quad + \ H$$
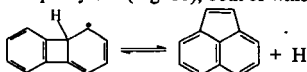
4. CONCLUSIONS

In conclusion, it can be stated that the kinetic model developed in the present work shows at least encouraging prediction capabilities for the first steps in the growth process to larger and larger polycyclic aromatic hydrocarbons. In particular, its satisfactory performance for two

different fuels and pressures increases its value for potential practical application. In next steps, the model will be extended to larger PAH, including up to eight aromatic rings, and a soot formation model will be implemented.

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